

# Synthesis, solid-state and solution structures of tris[(2-methoxymethyl)phenyl]germanes with a substituent on germanium<sup>☆</sup>

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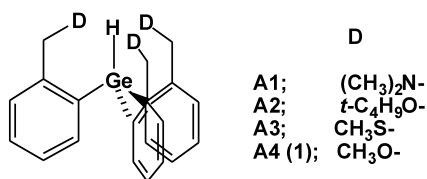
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**Abstract**—A series of tris[(2-methoxymethyl)phenyl]germanes with a substituent on germanium was prepared and their solid-state and solution structures were investigated by means of X-ray crystallography and NMR spectroscopy to elucidate the effect of the substituent on the hypercoordination of the germanium atom in triarylgermanes. It was shown that when the substituent is a halogen, the triarylgermanes tend to be pentacoordinated trigonal bipyramidal while the triarylgermane is tetrahedral with no coordination when the substituent is a phenyl group. The methyl derivative is a monocapped tetrahedron.

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## 1. Introduction

Hypercoordination (or hypervalency) is one of the most intriguing problems in the chemistry of organic compounds containing group 14 elements such as silicon, germanium or tin.<sup>1</sup> A particularly interesting family of compounds is triarylgermanes of general type **A**, where D is a donor atom such as nitrogen.



triarylgermanes **A**

The first compound which attracted our attention was tris[(2-dimethylaminomethyl)phenyl]germane (**A1**), reported by Corrieu et al.<sup>2,3</sup> **A1** is heptacoordinated, and is a tricapped tetrahedron where the three carbon atoms bonded to germanium and the hydrogen atom form a tetrahedron with the germanium atom at the core, and three

nitrogen atoms coordinated with germanium from outside of the tetrahedron. The donor atom is bound to germanium anti to the C1 carbon atom (for numbering, see [Scheme 1](#)).

Judging from the N–Ge distances, the coordination is strong although the electrophile (Ge) is not necessarily activated by an electron acceptor such as a halogen atom. We were interested to delineate the scope of this type of coordination in structure **A**. With this in mind, in a previous communication, we prepared tris[(2-*t*-butoxymethyl)phenyl]germane (**A2**; D=*t*-BuO) and tris[(2-methylthiomethyl)phenyl]germane (**A3**; D=SMe) and determined their solid state structure by means of X-ray crystallography.<sup>4</sup>

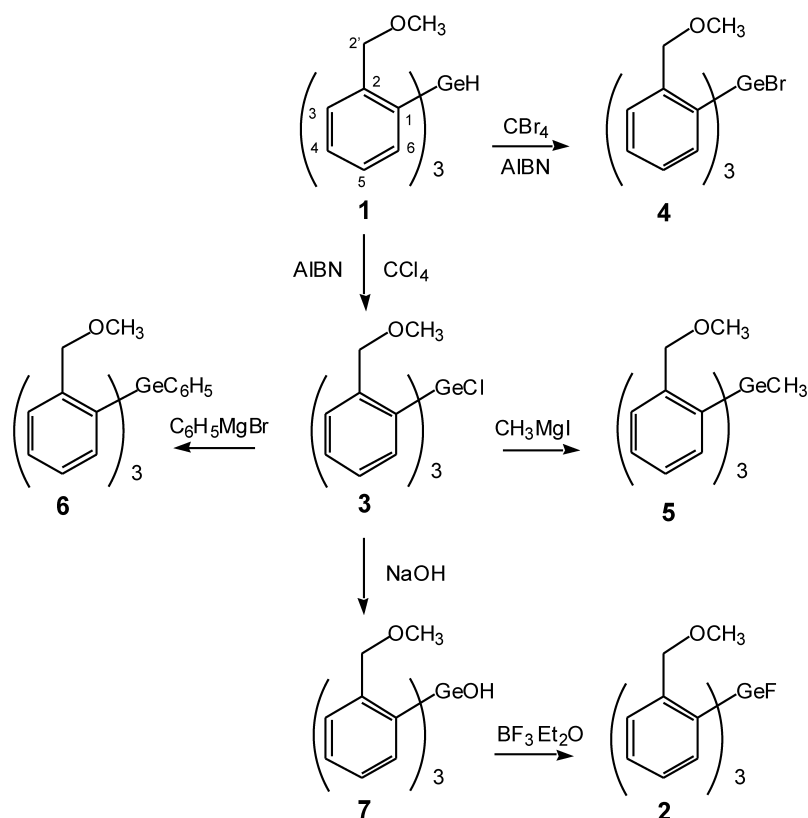
We found that **A2** is hexacoordinated (i.e. dicapped tetrahedron) while **A3** is heptacoordinated (i.e. tricapped tetrahedron). The fact that **A2** is hexacoordinated rather than heptacoordinated is probably due to the larger steric requirement of the *t*-Bu group. Thus, coordination of two *t*-BuO groups to germanium would leave little space for the third *t*-BuO to approach the germanium atom. Unfortunately, we failed to obtain tris[(2-methoxy)phenyl]germane (**A4**; D=OMe) in good crystalline form.

During this investigation, it occurred to us that it would be interesting to introduce a substituent other than hydrogen onto germanium atom. The presence of the substituent is expected to affect the hypercoordination of the germanium atom because of its steric requirement while the electronic effect of the substituent may also perturb the Lewis acidity of the germanium atom. With this in mind, we prepared a

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**Keywords:** organogermanium compounds; hypercoordination; triarylgermane; Ge-73 NMR; variable temperature H-1 NMR.

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**Scheme 1.** Synthesis of triarylgermanes (2–7).

series of substituted tris[(2-methoxymethyl)phenyl]germanes, and investigated their solid-state and solution structures in order to elucidate the effect of substituents bonded to germanium atom on the hypercoordination of type A compounds. We chose, as the donor, the methoxy group rather than the dimethylamino group, which is stronger as the donor. The dimethylamino group is so large that the steric requirement of the substituent bonded to germanium may be obscured.

## 2. Results and discussion

### 2.1. Preparation of triarylgermanes

Compounds 2–6 were prepared from tris[(2-methoxymethyl)phenyl]germane (1). The synthesis of 1 has been described previously.<sup>4</sup>

Chlorotris[(2-methoxymethyl)phenyl]germane (3) was prepared by the reaction of 1 and carbon tetrachloride in the presence of a catalytic amount of AIBN. In the case of the synthesis of 3, it is possible to isolate the compound that was formed as the intermediate in the preparation of 1. The purity of the compound thus obtained was rather poor, so we chose to prepare 3 from pure 1. The fluoride, fluorotris[(2-methoxymethyl)phenyl]germane (2), was prepared from chlorotris[(2-methoxymethyl)phenyl]germane (3) via the hydroxide, tris[(2-methoxymethyl)phenyl]germyl hydroxide (7).

In the case of the bromide, bromotris[(2-methoxymethyl)phenyl]germane (4), the conventional method of bromina-

tion of 1 using NBS<sup>5</sup> was not effective, probably because of oxidation. Bromination with bromine was also unsuccessful. Use of a milder reagent, carbon tetrabromide, gave the desired 4 in very good yield. The preparation of tris[(2-methoxymethyl)phenyl]methylgermane (5) and tris[(2-methoxymethyl)phenyl]phenylgermane (6), were achieved by the reaction between 3 and an appropriate Grignard reagent. The results are summarized in Scheme 1.

All compounds prepared were characterized by X-ray crystallography except 7 which failed to give a good single crystal, as well as <sup>1</sup>H and <sup>13</sup>C NMR, mass spectroscopy and elemental analysis. The results were consistent with the expected structures.

### 2.2. X-Ray crystallographic analysis

Important geometric parameters obtained from X-ray crystallographic analysis of 2, 3, 4, 5 and 6 are summarized in Table 1.

#### 2.2.1. Molecular structure of halogermanes (2–4). An ORTEP drawing of the fluoride (2) is shown in Figure 1.

At first glance, it seems to be a tetrahedron. Careful examination of the drawing will, however, reveal that one of the oxygen atom (O1) approaches to germanium from behind the fluorine atom, and that three *ipso* carbon atoms form a triangle, to which F–Ge–O(1) axis is almost perpendicular. Thus, 2 has a somewhat twisted TBP structure with two apical Ge–F and Ge–O(1) bonds and three equatorial Ge–C bonds. The F–Ge–O(1) angle is 171.20°, deviating from the ideal value of 180° for a TBP to

**Table 1.** Geometric parameters of **2–6** in Å and °<sup>aa</sup>

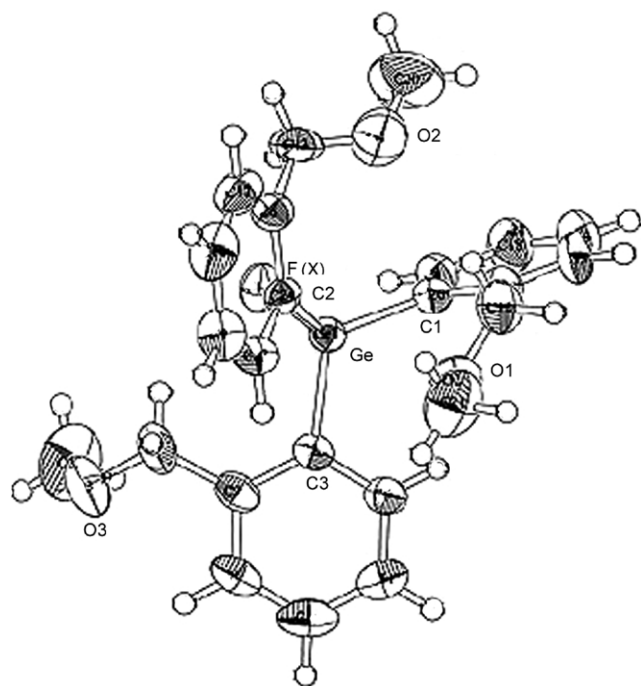
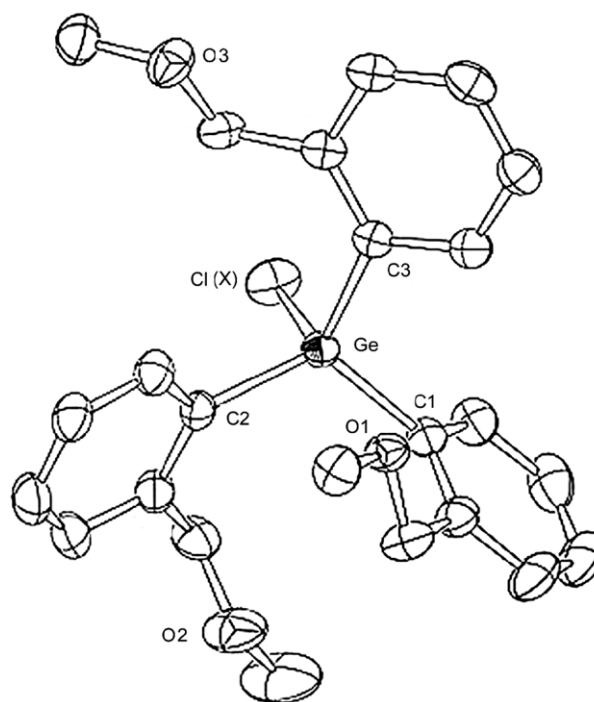
Compound	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
X	F	Cl	Br	Me	Ph
Ge–X	1.776(2)	2.2131(8)	2.3618(5)	1.954(3)	1.926(6)
Ge–O1	2.85	2.75	2.85	3.15	4.55
Ge–O2	3.47	4.09	4.62	4.13	4.58
Ge–O3	4.63	4.63	4.68	4.62	4.6
Ge–C1	1.936(3)	1.946(3)	1.961(4)	1.959(3)	1.936(6)
Ge–C2	1.937(3)	1.952(3)	1.956(4)	1.954(3)	1.938(6)
Ge–C3	1.947(3)	1.954(3)	1.937(4)	1.954(3)	1.948(6)
X–Ge–O1	172.1	173.7	172.2	168.8	–
X–Ge–C1	100.3(1)	112.2(1)	103.0(1)	106.9(1)	112.2(3)
X–Ge–C2	102.0(1)	102.83(9)	103.6(1)	108.9(1)	109.6(3)
X–Ge–C3	102.4(1)	103.17(9)	104.2(1)	108.0(1)	105.8(2)
C1–Ge–C2	121.8(1)	116.6(1)	115.1(2)	110.4(1)	109.0(2)
C2–Ge–C3	115.6(1)	117.0(1)	116.4(1)	112.9(1)	107.7(2)
C3–Ge–C1	110.8(1)	112.2(1)	112.5(2)	109.5(1)	112.4(3)
% TBP	46.1	52.1	46.1	28.1	–

<sup>a</sup> Atom labels O1, O2, O3, C1, C2 and C3 correspond to the those in Figures 1–5.

some extent. Deviation of ca. 10° is common with this type of pentacoordinate structures.<sup>6</sup>

The distances between the three oxygen atoms O(1), O(2) and O(3) and germanium are, respectively, 2.85, 3.47 and 4.69 Å. The first one is much shorter than the sum of the van der Waals radii of oxygen and germanium, 3.62 Å, and is shorter than the corresponding value for **A2** (ca. 3.2–3.3 Å). This will indicate a strong interaction between O(1) and germanium atom. The second value is also shorter than 3.62 Å, demonstrating the existence of a weak interaction between O(2) and germanium. Hence, **2** is hexacoordinated. So, **2** may be said to have a unique monocapped TBP structure.

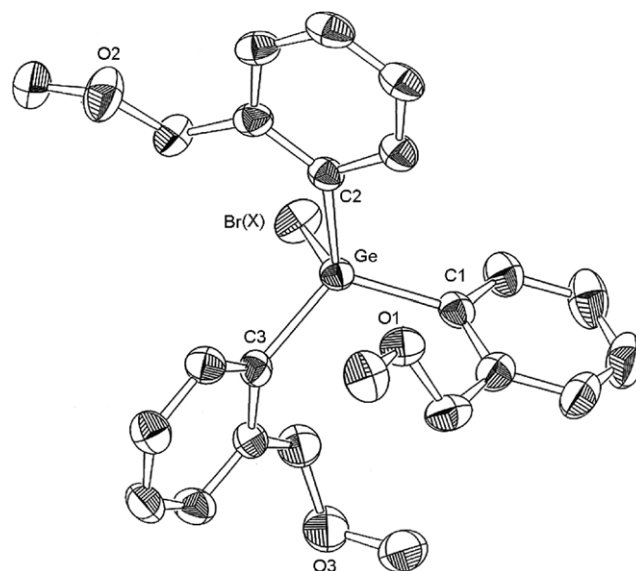
Figure 2 shows an ORTEP drawing of **3**. The structural parameters in Table 1 are very similar with those of **2** except

**Figure 1.** ORTEP drawing of **2**. Atom labels correspond to those in Table 1.**Figure 2.** ORTEP drawing of **3**. Atom labels correspond to those in Table 1.

the values for Ge–O distances. Thus, **3** has also a TBP structure. As only one of the methoxy oxygen coordinates with germanium (the Ge–O1 distance is 2.75 Å) while the other two methoxy groups are away from germanium (Ge–O2 and Ge–O3 bond lengths >4 Å), we can conclude that **3** is pentacoordinate TBP without any additional coordination from O2 or O3.

The ORTEP drawing of **4** is given in Figure 3.

The structure of **4** is similar to that of **3**, a twisted TBP. Thus, one of the MeO oxygen coordinates with germanium (the Ge–O1 distance is 2.85 Å) while the other two methoxy groups are away from germanium (Ge–O2 and

**Figure 3.** ORTEP drawing of **4**. Atom labels correspond to those in Table 1.

Ge–O3 bond lengths  $>4.5 \text{ \AA}$ ). The Ge–Br and Ge–O(1) bonds are apical with three Ge–C equatorial bonds.

Of the three halides **2**, **3** and **4**, only **2** has two Ge–O distances shorter than the sum of the van der Waals radii of oxygen and germanium, e.g.  $3.62 \text{ \AA}$ , and the sum of the differences between the Ge–O distance and  $3.62 \text{ \AA}$  amounts to  $0.92 (=0.77+0.15) \text{ \AA}$ . For **3** and **4**, only one Ge–O distance is shorter than  $3.62 \text{ \AA}$ , and the differences are  $0.87$  and  $0.77 \text{ \AA}$ , respectively. Thus, the three values decrease in the order  $\mathbf{2} < \mathbf{3} < \mathbf{4}$ , which seems to reflect the electronegativity of halogens.

**2.2.2. % TBP character.** There are several ways to estimate the extent of TBP character in a pentacoordinated species. The angle made by axial substituent–central atom–axial substituent ( $180^\circ$  for a perfect TBP) is one example.

Another method of determining the extent of the TBP character is to compare the difference between the central atom–donor distance and the sum of the van der Waals covalent radii. In this case, the measure of structural feature is to calculate the extent to which the Ge–O donor distance has changed from the van der Waals sum of  $3.62 \text{ \AA}$  compared to the sum of the covalent radius of Ge and O,  $1.96 \text{ \AA}$ . This method has successfully been used for cyclic silanes by Holmes et al.<sup>7</sup> Values of the percent trigonal bipyramidal character (% TBP) obtained in this manner are listed in Table 1.

In the case of cyclic silanes investigated by Holmes et al., many compounds have % TBP values similar with those of **2–4**. However, if the central atom (Si) is substituted by halogens, the % TBP tends to be larger. This may in turn indicate that factors determining % TBP are various, and the electronegativity of the substituent on the host atom is one important factor determining the structure of hyper-coordinated species.

The reason why **2–4** have a TBP structure, rather than a tetrahedral one as **A2**, may also be various. One possible reason is the electronegativity of the halogen atoms, particularly of the fluorine atom, which should enhance the Lewis acidity (i.e. electrophilicity) of germanium. This enhanced Lewis acidity will favor formation of a Ge–O interaction that is stronger in a TBP structure than in capped tetrahedron.

The second possible reason is the bulkiness of the halogen atoms as compared with that of hydrogen in **1**. It is likely that the presence of a halogen atom on germanium will make the approach of side chain oxygen to germanium difficult.

It must be pointed out that the apical Ge–X distances of **2**, **3** and **4** remain in the normal bond lengths of this kind.

**2.2.3. Molecular structure of methylgermane (5).** Figure 4 presents an ORTEP drawing of **5**.

The values of three Ge–O distances indicate that one oxygen coordinates with the germanium and the other two oxygen atoms are far removed from it. Thus **5** is

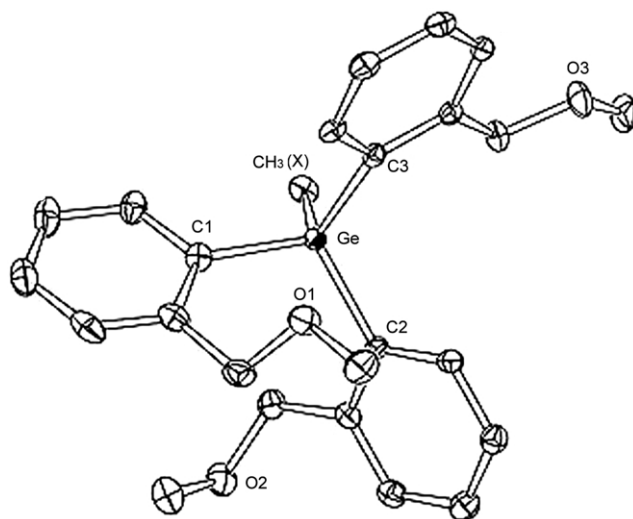


Figure 4. ORTEP drawing of **5**. Atom labels correspond to those in Table 1.

pentacoordinated. The three Ar–Ge–Ar angles as well as three C(Me)–Ge–Ar angles are all close to  $109.5^\circ$ , the tetrahedral angle, which is a good indication that **5** is monocapped tetrahedron. Hence, % TBP is much smaller than those of **2**, **3** and **4**. Since the steric requirement of a methyl group is similar to that of a chlorine atom, it seems that the difference in the % TBP between **3** and **5** is due to the difference in electronegativity.

**2.2.4. Molecular structure of phenylgermane (6).** An ORTEP drawing of **6** is given in Figure 5.

All three Ge–O distances are larger than the sum of the van der Waals radii of Ge and O, and furthermore, each of the lone pair of oxygen atoms is directed away from the germanium. All Ar–Ge–Ar and C(Ph)–Ge–Ar angles are close to the tetrahedral angle, indicating that **6** is essentially

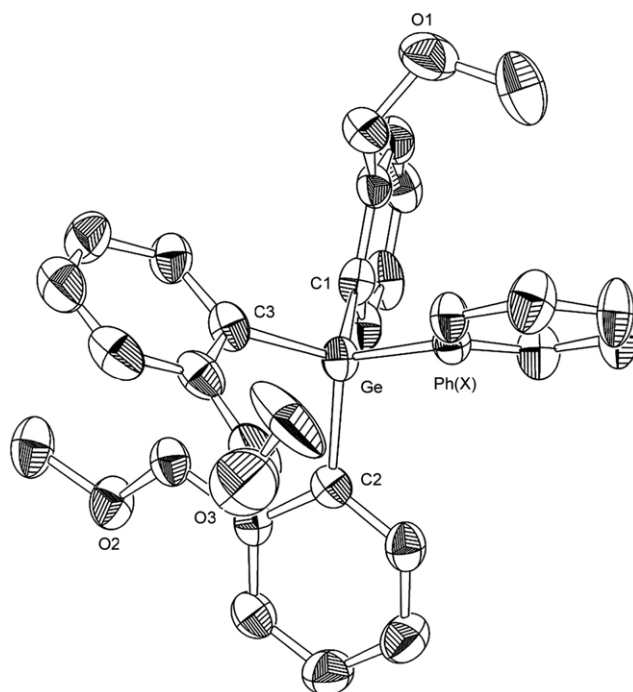


Figure 5. ORTEP drawing of **6**. Atom labels correspond to those in Table 1.

**Table 2.**  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) data of **2–7** in  $\text{CDCl}_3$ <sup>a</sup>

Compounds	OMe	C2'	C1	C2	C3	C4	C5	C6	Substituent
<b>2</b>	57.92	74.09 <sup>b</sup>	134.69 <sup>c</sup>	143.59	127.40	127.10	129.97	135.90 <sup>c</sup>	–
<b>3</b>	57.69	73.83	134.96	143.33	127.74	126.97	129.89	135.12	–
<b>4</b>	57.98	74.06	134.96	143.50	128.16	127.25	130.21	135.64	–
<b>5</b>	58.07	74.91	137.23	143.61	128.30	127.26	129.25	135.41	1.54
<b>6</b>	58.16	74.98	137.72	144.57	128.59	127.73	129.15	135.84	128.5 130.00 135.09 135.65
<b>7</b>	57.81	74.84	136.73	143.36	128.77	127.45	129.82	135.47	–

<sup>a</sup> For numbering, see Scheme 1, compound **1**.

<sup>b</sup> Doublet; ( $^4J(^{19}\text{F}-^{13}\text{C})=1.68$  Hz).

<sup>c</sup> Doublet; ( $^2J(^{19}\text{F}-^{13}\text{C})=14.10$  Hz), c doublet; (d;  $^3J(^{19}\text{F}-^{13}\text{C})=4.15$  Hz).

tetrahedral with no coordination of the side-chain oxygen. This is in line with the larger size of the phenyl group in **6** as compared with the that of the methyl group in **5**.

The symmetrical structure of **6** is supported by its  $^{73}\text{Ge}$  NMR spectrum, which will be described in the following section.

### 2.3. NMR spectroscopic study

**2.3.1.  $^{13}\text{C}$  NMR spectra.** We were interested to see whether the structures of **2–5** in solution reflect the hypercoordination observed in the solid state. In Table 2,  $^{13}\text{C}$  NMR data of **2–6** are summarized. The assignment was made based on the data of previously reported compounds.<sup>4</sup>

The most crucial point is whether the C2' shifts reflect the extent of coordination of the side-chain with germanium. The chemical shift range for C2' is small (ca. 1 ppm) and hence it is difficult to use this shift as a criterion for determining coordination. Since we observed only one sharp signal for C2', a rapid equilibrium between the coordinated and uncoordinated species is observed at ambient temperature.

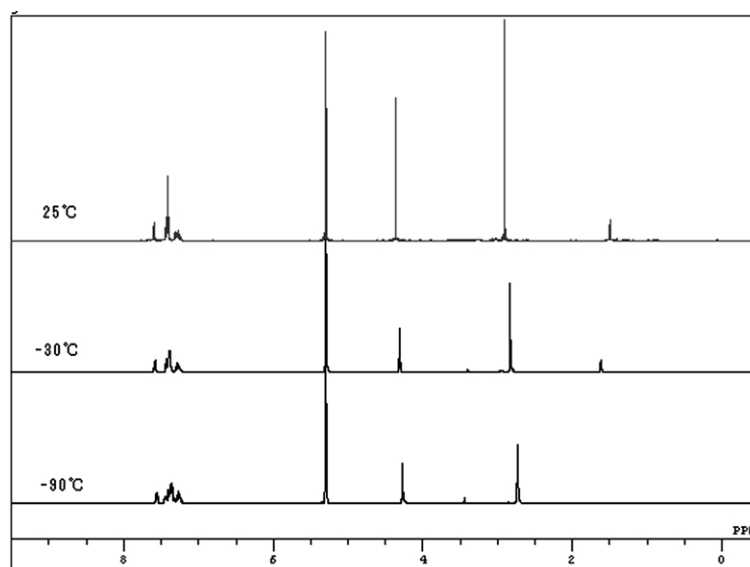
**2.3.2.  $^1\text{H}$  NMR spectra.** As we expected that the

equilibrium between coordinated and uncoordinated- $\text{CH}_2\text{OCH}_3$  moiety is slowed down at lower temperatures, we carried out a variable temperature  $^1\text{H}$  NMR study of **2** and **3**. Compounds **2** and **3** were chosen because the Ge–O interaction in these compounds will be stronger due to the enhanced Lewis acidity of germanium.

Figures 6 and 7 present the variable temperature  $^1\text{H}$  NMR spectra of **2** and **3**. For the fluoride, **2**, we observed no splitting down to  $-90^\circ\text{C}$ . For the chloride, **3**, the signals due to  $-\text{OCH}_3$  and  $-\text{CH}_2\text{O}-$  broaden below  $-30^\circ\text{C}$ , which might indicate the structure with one coordinated  $-\text{CH}_2\text{OCH}_3$  moiety is gradually freezing.

Unfortunately, further reasoning of this broadening was impossible because the solution became excessively viscous upon further lowering of the temperature.

**2.3.3.  $^{73}\text{Ge}$  NMR spectra.** Since  $^{73}\text{Ge}$  nuclei are quadrupolar, their NMR signal tends to be excessively broad, and signal recording is usually possible only when the electric field gradient around germanium is highly symmetric. We have shown, however, that the linewidth may be correlated with the hypercoordination of germanium.<sup>8</sup> Thus, the signal is broader when the germanium is penta- or hexavalent. Among compounds **2–6**, it is expected that only **5** and **6** will



**Figure 6.** Variable temperature  $^1\text{H}$  NMR spectra of **2** in  $\text{CH}_2\text{Cl}_2$ .

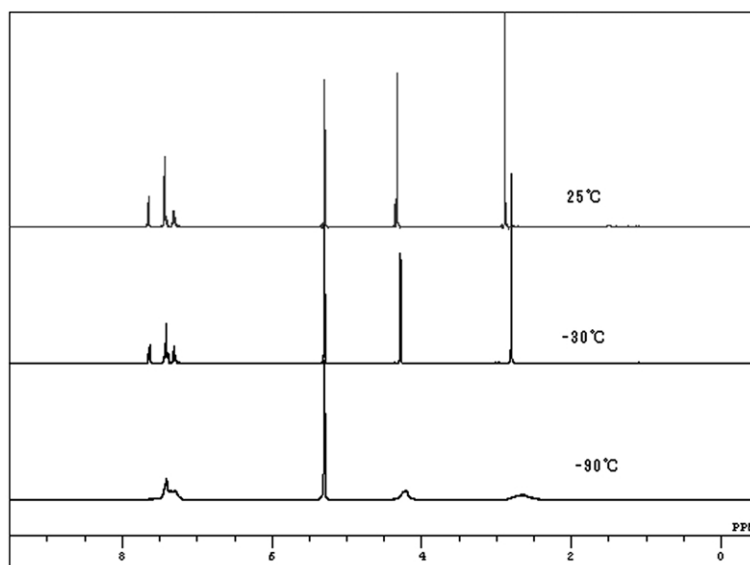


Figure 7. Variable temperature  $^1\text{H}$  NMR spectra of **3** in  $\text{CH}_2\text{Cl}_2$ .

give detectable signals. In fact **6** gave a sharp signal (half width, 75 Hz), which is in good agreement with its tetrahedral structure without any further coordination.

The effect of the phenyl group on  $^{73}\text{Ge}$  chemical shift (ca. 48 ppm for **1** and **6**) is comparable with that for related compounds (ca. 25 ppm for tri- and tetra-phenylgermane). The relevant data are summarized in Table 3.

Table 3.  $^{73}\text{Ge}$  NMR chemical shifts and linewidths of some arylgermanes in  $\text{CDCl}_3$ <sup>a</sup>

	$\delta$ (ppm)	Half-width (Hz)	Ref.
<b>1</b>	−85.4	350	9
<b>6</b>	−27.8	75	This study
Triphenylgermane	−56.0	87	9
Tetraphenylgermane	−32.6	6	9

<sup>a</sup> Chemical shift ( $\delta$ ) relative to external tetramethylgermane.

### 3. Conclusion

A series of substituted tris[(2-methoxymethyl)phenyl]germane (**2–6**) were prepared and their solid state structure were investigated by X-ray crystallographic analysis. The structure varies from a monocapped TBP, TBP, mono-capped tetrahedron and tetrahedron as the substituent varies from F, Cl, Br, Me to Ph.

The structure of three halotriarylgermanes was disclosed by X-ray crystallographic analysis. All of three have a TBP structure. This is in line with an enhanced Lewis acidity of germanium atom. The importance of the nature of substituent on germanium, and particularly, the Lewis acidity of germanium has a very important role in determining the structure of triarylgermanes.

Thus, methyltriarylgermane is a monocapped tetrahedron similar with previously reported triarylgermane (i.e. the substituent is H), while phenyltriarylgermane is now a genuine tetrahedron, indicating that in this case perhaps steric factor is predominant.

To conclude, the extent of hypercoordination of triarylgermanes depends on a variety of factors including the type of donor atom, the bulkiness of the substituent on the donor, and probably most importantly, the size and nature of the substituent atom on germanium.

The exchange of coordinated and uncoordinated site could not be frozen even at  $-90^\circ\text{C}$  which is the limit attained by the variable temperature NMR study.  $^{73}\text{Ge}$  spectrum of **6** confirmed it tetrahedral structure.

## 4. Experimental

### 4.1. Syntheses

Mps were obtained using a YANACO MP-S3 apparatus and are uncorrected. IR spectra were recorded using an FTIR-8300 (Shimadzu) spectrophotometer.  $^1\text{H}$  NMR spectra were determined in  $\text{CDCl}_3$  solution with a JEOL ECP-500 (500 MHz) or JEOL EX-400 (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard.  $J$  values are given in Hz.  $^{13}\text{C}$  NMR spectra were determined in  $\text{CDCl}_3$  solution using JEOL ECP-500 operating at 125.65 MHz, using TMS as internal standard.  $^{19}\text{F}$  NMR were determined with the same instrument operating at 470.4 MHz with  $\text{CFCl}_3$  as an external standard.  $^{73}\text{Ge}$  NMR spectra were determined with the same instrument operating at 17.44 MHz with tetramethylgermane as an external standard (condition of measurement; data points, 2048; spectral width, 12500 Hz; acquisition time, 0.1638 s).

Column chromatography was carried out with Wakogel C-200. High pressure liquid chromatography was carried out with LC-908-G30 (Japan Analytical Industry) with JAIGEL-2H (GPC column, Japan Analytical Industry) and JAYGEL-ODS (ODS column, Japan Analytical Industry).

**4.1.1. Tris[(2-methoxymethyl)phenyl]germane (1).** The compound was prepared by the method described in the previous paper.<sup>4</sup> The reaction between the Grignard reagent

of 2-bromo-1-methoxymethylbenzene and  $\text{GeCl}_4$  afforded **1** in 21.3% yield, mp 68–70°C (from hexane or diethyl ether).

#### 4.1.2. Chlorotris[(2-methoxymethyl)phenyl]germane (**3**).

To a  $\text{CCl}_4$  solution (100 ml) of **1** (0.54 g, 1.3 mmol) was added 2 mg of AIBN, and refluxed for 7 h under  $\text{N}_2$ .<sup>9</sup> After refluxing, the solvent was removed and the residue was purified by GPC (SL;  $\text{CHCl}_3$ ) to give **3**, (0.42 g, 76.3%) as colorless crystals.

**Compound 3.** Mp 98–100°C (from hexane/dichloromethane). (Found: C 60.81; H 5.67; Cl 7.93%.  $\text{C}_{24}\text{H}_{27}\text{ClGeO}_3$  requires C, 61.13; H 5.77; Cl 7.51%. %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , rt); 3.11 (s, 9H, OMe), 4.43 (s, 6H,  $\text{PhCH}_2\text{O}$ ), 7.18–7.43 (m, 3H, aromatic).

#### 4.1.3. Bromotris[(2-methoxymethyl)phenyl]germane (**4**).

To the hexane solution (50 ml) of **1** (0.51 g, 1.1 mmol) was added 0.36 g of carbon tetrabromide (1.1 mmol) and 2 mg of AIBN, and the mixture was refluxed for 2 h under  $\text{N}_2$ . Then the solvent was removed, and the residue was purified by GPC (SL;  $\text{CHCl}_3$ ) to give **4** (0.42 g, 74.0%) as colorless crystals.

**Compound 4.** Mp 99–100°C (from hexane). (Found: C, 55.75; H, 5.37%.  $\text{C}_{24}\text{H}_{27}\text{BrGeO}$  requires C, 55.87; H, 5.27%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , rt); 2.94 (9H, s,  $\text{OCH}_3$ ), 4.39 (6H, s,  $\text{ArCH}_2\text{O}$ ), 7.31–7.71 (12H, m, aromatic).

#### 4.1.4. Tris[2-(methoxymethyl)phenyl]methylgermane (**5**).

The Grignard reagent was prepared from methyl iodide (0.4 g, 2.8 mmol) and magnesium (0.06 g, 2.4 mmol) in dry diethyl ether (5 ml). To this solution there was dropwise added a diethyl ether solution (10 ml) of **3** (0.15 g, 0.32 mmol), and refluxed for 8 h. After cooling at 0°C, hydrochloric acid (2 mol/dm<sup>3</sup>, 15 ml) was added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and dried over

anhydrous magnesium sulfate. After removing the solvent, the residue was purified by GPC (SL;  $\text{CHCl}_3$ ) to give **5** (0.10 g, 69.3%) as colorless crystals.

#### 4.1.5. Tris[(2-methoxymethyl)phenyl]phenylgermane (**6**).

The Grignard reagent was prepared from bromobenzene (1.35 g, 8.2 mmol) and magnesium (0.19 g, 8.2 mmol) in dry diethyl ether (10 ml). To this solution there was dropwise added a diethyl ether solution (10 ml) of **3** (0.29 g, 0.63 mmol) and the mixture was refluxed for 1 h. The solvent was exchanged to toluene (30 ml), and the toluene solution was further refluxed for 10 h. After cooling to rt, the mixture was decomposed by hydrochloric acid (2 mol/dm<sup>3</sup>, 30 ml). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the residue was purified by GPC (SL;  $\text{CHCl}_3$ ) to give **7** (0.12 g, 36.5%) as colorless crystals.

#### 4.1.5. Tris[(2-methoxymethyl)phenyl]phenylgermane (**6**).

The Grignard reagent was prepared from bromobenzene (1.35 g, 8.2 mmol) and magnesium (0.19 g, 8.2 mmol) in dry diethyl ether (10 ml). To this solution there was dropwise added a diethyl ether solution (10 ml) of **3** (0.29 g, 0.63 mmol) and the mixture was refluxed for 1 h. The solvent was exchanged to toluene (30 ml), and the toluene solution was further refluxed for 10 h. After cooling to rt, the mixture was decomposed by hydrochloric acid (2 mol/dm<sup>3</sup>, 30 ml). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the residue was purified by GPC (SL;  $\text{CHCl}_3$ ) to give **7** (0.12 g, 36.5%) as colorless crystals.

**Compound 6.** Mp 110–111°C (from hexane). (Found: C, 70.10; H, 6.36%.  $\text{C}_{30}\text{H}_{32}\text{GeO}_3$  requires C, 70.21; H, 6.28%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , rt) 2.85 (9H, s,  $\text{OCH}_3$ ), 4.11 (6H, s,  $\text{ArCH}_2\text{O}$ ), 7.24–7.56 (17H, m, aromatic).

#### 4.1.6. Hydroxytris[(2-methoxymethyl)phenyl]germane (**7**).

The benzene solution (30 ml) of **3** (0.1 g, 0.21 mmol) was added to aq. NaOH (30 ml, 2 mol/dm<sup>3</sup>), and the mixture was refluxed for 3 h. After cooling to rt, the mixture was extracted with benzene and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was recrystallized with hexane to afford **8** (0.09 g, 94.8%) as colorless crystals.

**Table 4.** Crystal data for compounds 2–6

Compounds	2	3	4	5	6
Formula	$\text{C}_{24}\text{H}_{27}\text{FgeO}_3$	$\text{C}_{24}\text{H}_{27}\text{ClGeO}_3$	$\text{C}_{24}\text{H}_{27}\text{BrGeO}_3$	$\text{C}_{27}\text{H}_{30}\text{GeO}_3$	$\text{C}_{30}\text{H}_{32}\text{GeO}_3$
Formula weight	442.97	471.5254	515.97	451.1	513.17
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal color	Colorless	Colorless	Colorless	Unknown	Colorless
Crystal size (mm)	0.3×0.3×0.3	0.2×0.2×0.3	0.2×0.2×0.15	0.1×0.1×0.1	0.15×0.1×0.07
<i>a</i> (Å)	8.3625(3)	15.208(1)	9.3798(6)	9.277(1)	9.136(2)
<i>b</i> (Å)	16.1375(7)	9.4869(5)	11.05861(1)	11.0097(8)	11.708(3)
<i>c</i> (Å)	16.8671(7)	16.0028(5)	11.5549(7)	00.4459(9)	13.097(2)
$\alpha$ (°)			98.653(2)	98.576(3)	99.367(2)
$\beta$ (°)	101.984(1)	105.177(2)	92.830(4)	93.064(3)	103.626(1)
$\gamma$ (°)			110.834(3)	111.505(4)	107.856(7)
<i>V</i> (Å <sup>3</sup> )	2226.6(2)	22269.0(2)	110.55(10)	1068.1(2)	125303(5)
<i>Z</i>	8	4	2	2	2
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.643	1.405	1.557	1.403	1.36
$\lambda$ (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
$\mu$ (mm <sup>-1</sup> )	28.06	15.15	32.34	14.57	12.51
$2\theta_{\text{max}}$ (°)	54.8	55.0	55.1	55	55.3
Number of reflections refined	5058	3588	4927	4049	5587
Number of parameters	262	262	262	262	307
<i>R</i> (on <i>F</i> for obs. refls.)	0.044	0.037	0.050	0.045	0.084
<i>R</i> <sub>w</sub> (on <i>F</i> for obs. refls.)	0.12	0.047	0.142	0.132	0.207
GOF	1.56	1.28	2.01	1	2.17

**Compound 7.** Mp 72.0–74.5°C (from hexane). (Found: C, 63.56; H, 6.26%.  $C_{24}H_{28}GeO_4$  requires C, 63.62; H, 6.23%).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ , rt) 3.08 (9H, s,  $OCH_3$ ), 4.41 (6H, s,  $ArCH_2O$ ), 7.26–7.50 (17H, m, aromatic).

#### 4.1.7. Fluorotris(2-methoxymethyl)phenylgermane (2).

The anhydrous acetonitrile solution (10 ml) of **7** (0.1 g, 0.24 mmol) was dropwise added to anhydrous acetonitrile solution (5 ml) of boron trifluoride diethyl ether complex (1.43 g, 1.25 mmol) at 50°C under  $N_2$ , and stirring was continued for another 12 h.<sup>10</sup> After cooling, methanol (20 ml) was added to the mixture. After removing the solvent, the residue was extracted with  $CH_2Cl_2$  and the organic layer was dried over anhydrous magnesium sulfate. The residue, after removing solvent, was purified by recrystallization from hexane to give **2**.

**Compound 2.** Mp 118–119°C (from hexane). (Found C, 63.09; H, 6.07%.  $C_{24}H_{27}FGeO_3$  requires C, 63.34; H, 5.98%).  $^1H$  NMR; ( $CDCl_3$ ,  $\delta$ , rt) 2.95 (9H, s,  $OCH_3$ ), 4.41 (6H, s,  $ArCH_2O$ ), 7.29–7.66 (12H, m, aromatic);  $^{19}F$  NMR; ( $CDCl_3$ ,  $\delta$  relative to  $CF_3COOH$ , rt) –155.01.

#### 4.2. X-Ray data collection and reduction

Crystal data from **2–7** were collected at rt on a Rigaku RAXIS-RAPID Imaging Plate four-circle diffractometer. Intensity data were collected by the  $\theta/2\theta$  scan techniques. Structures were solved by direct methods using the programs SIR 92. Structures were refined by full-matrix least-squares interactions. Final atomic parameters were deposited at the Cambridge Crystallographic Data Centre.<sup>11</sup> The crystallographic data are summarized in Table 4. Perspective views of the molecules (Figs. 1–5) were made by the use of ORTEP for teXsan.<sup>12</sup>

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